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COMPLETE SPECIFICATION

Improvements relating to Curable Chlorinated Polyethylene Compositions and Their Use

We, ALLIED CHEMICAL CORPORATION, a Corporation organized and existing under the laws of the State of New York, United States of America, of 61, Broadway, New York 6, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to curable chlorinated polyethylene compositions and to the bonding of plastics therewith.

Chlorinated polyethylene is a well known material produced generally by subjecting an ethylene polymer to the action of elemental chlorine. The chlorinated polyethylene is apparently relatively simple in structure, but can vary greatly in performance and properties depending on several factors including chlorine content and method of chlorination. Chlorinated polyethylene containing about 15—50% chlorine are suitable for use as elastomers upon curing with an agent such as an organic peroxide or polyfunctional amine. (All proportions are by weight unless otherwise stated). However, the elastomers so produced have been troublesome and deficient with respect to certain properties, and their suitability for use in a number of important elastomer applications has been accordingly restricted. Important properties in which the cured chlorinated polyethylene elastomers have left room for improvement include tensile strength, elongation, compression set, water resistance, resistance to heat aging and oil aging, processability, and moulding and extrusion properties.

The compositions of the present invention comprise (a) a chlorinated polyethylene, which is a homopolymer of ethylene or a copolymer of ethylene with up to 15 percent by weight of propylene or butylene and which contains 15 to 50 percent by weight of the chlorine, (b) at least 0.5 percent (based on the weight of the chlorinated polyethylene) of an organic compound containing at least two terminal ethylenically unsaturated groups each of formula $-\overset{|}{\underset{|}{C}}-CR=CH_2$ or $-\underset{\|}{C}-CR=CH_2$, in which R is hydrogen or an alkyl group, which, at least in the proportion employed, is compatible with the chlorinated polyethylene, and (c) a free radical-generating initiator for addition polymerisations.

These compositions may be cured under heat and pressure. The cured chlorinated polyethylene elastomers produced by the process of the invention are better in a number of respects than peroxide and amine-cured chlorinated polyethylenes proposed in the past, especially in a desirably high degree of cure or cross-link density. The cured compositions may contain polymerized products of the terminally unsaturated (allylic) co-agent, but we do not wish to be limited to any exact theory or explanation inasmuch as the high degree of improvement and excellent overall properties of the cured compositions suggest a highly effective combination of

mechanisms including cross-linking of the chlorinated polyethylene directly and also possibly through the unsaturated monomer or a polymer thereof. It has been found that the good overall properties of the cured compositions make them well suited for use in a number of important elastomer applications, such as gaskets, hose and wire coating. Specific properties especially improved include tensile strength, compression set, heat and oil aging resistance, and extrudability. The improvement in tensile strength is exhibited primarily in compositions not containing the larger amounts of filler, while compositions having moderate or large filler content are noteworthy as retaining desirably low compression set. Elastomers and elastomer compositions in accordance with the invention also have other desired properties, including good processability, elongation, high modulus, improved moulding properties, colourability, solvent and oil resistance, water resistance, and good electrical insulating properties. It has been further found that filled compositions containing the allylic compounds may be extruded onto wire and cured without stress cracking of the cured coating, which has been a problem in the past with curable high molecular weight chlorinated polyethylene compositions. It has also unexpectedly been found that the incorporation of normally liquid allylic materials in chlorinated polyethylene stabilises it against heat decomposition, for example when working on a Banbury mixer or rubber mill, and the invention includes also the use of these compounds as stabilisers and processing aids for chlorinated polyethylene, whether or not the final composition is subjected to curing.

The chlorinated polyethylene (or more strictly ethylene polymer) (a) may be any chlorinated polymer of ethylene containing 0—15% by weight of propylene or butylene, having a chlorine content of 15% to 50% by weight, preferably 30—45%, and derived by low or moderate pressure catalytic polymerization of ethylene, for example in the presence of the well known Zeigler or Phillips catalysts at pressures up to about 5000 p.s.i. (350 kg/cm²). Desirably, the ethylene polymer is a linear, high density homopolymer. The terms "linear" or "substantially linear", as used herein mean that the polyethylene is of high density and has at most only nominal short chain branching in the form of methyl groups, usually less than about 10 methyl groups per 1,000 carbon atoms in the molecule, more commonly 0 to 5 methyl groups. The density of such polyethylene is at least 0.935 gr/cm³, usually 0.940 to 0.985 gr/cm³. The preferred chlorinated polyethylenes have a crystallinity of less than 10%, desirably 0%. The molecular weight of the chlorinated polyethylene may vary substantially, exceptionally good elastomers being obtained with a high molecular weight chlorinated polyethylene having an intrinsic viscosity between 2.5 and 6 as measured in *o*-dichlorobenzene at 100°C.

The organic compound (b) may be broadly termed an "allylic" compound or coagent; it contains at least two terminal ethylenically unsaturated groups as aforesaid, the carbon atom opposite the terminal methylene group optionally forming part of a ring structure, as for example in divinyl benzene. While the allylic compound will usually be monomeric, it can if desired be a low polymer.

The allylic coagent must also be compatable with the chlorinated polyethylene and polymerizable in the presence of a free radical initiator; examples are the allyl esters and ethers. The term "compatible" as used herein means fully miscible in the desired proportion with the chlorinated polyethylene to form a homogeneous mass upon mixing, for example on a rubber mill, after no more than 20 minutes at any processing temperatures up to 400°F. The coagent compound is desirably normally liquid, although solids may be used including non-thermoset prepolymers of diallyl phthalate or allylic compounds compatible with the chlorinated polyethylene at processing temperatures. Materials such as triallyl cyanurate are difficult to mix, but can be made compatible in effective proportions by mixing with a secondary plasticizer such as a chlorinated paraffin to form a binary mixture which is compatible. Representatives of the allylic compounds which may be employed include the allylic derivatives of phthalic acid and of the saturated and unsaturated aliphatic dibasic or tribasic acids of 2 to 12, especially 3—6, carbon atoms in all, including diallyl phthalate, diisoallyl phthalate, diallyl sebacate, diallyl maleate, diallyl fumarate, diallyl adipate and diallyl succinate. Examples of other useful allylic compounds are triallyl cyanurate and triallyl isocyanurate. A preferred allylic material is diallyl phthalate. Other suitable coagents include coesters which are essentially the reaction product of two or more mols of a terminally unsaturated acid and one mol of a polyhydric alcohol. Preferred unsaturated acids include acrylic acid, methacrylic acid, and ethacrylic acid, and the preferred polyhydric alcohols contain 2 to 12 carbon atoms and 2 to 4 hydroxy groups. Examples of such esters include ethylene glycol dimethacrylate, trimethylol propen dimethacrylate and 1,3-butylene glycol dimethacrylate. An example of an additional useful coagent differing from the above is divinyl benzene.

The amount of the coagent employed may vary widely depending largely on the particular coagent and on the end use of the

product. As little as 0.5 part of coagent per 100 parts of the chlorinated polyethylene is effective in improving the properties of the cured elastomer, and also in effecting at least a partial stabilization of chlorinated polyethylene against heat decomposition. The upper limit of the amount of coagent is not particularly critical, although 100 parts represents a practical upper limit from a cost and effectiveness standpoint. The optimum amount of the allylic compound generally depends upon the particular end use and properties desired for the cured product. Amounts between 7 and 15 parts of the allylic compound per 100 parts of the chlorinated polyethylene are preferable in producing compositions for use as low cost wire jacketing or in other applications where very low compression set is not critical but tensile strength, elongation, modulus, extrudability, high cure, colourability, water and oil resistance, and electrical insulating properties are important. Compositions containing 15 to 70 parts of the allylic compound are preferably employed to produce products having particularly low compression set, generally less than 35%, usually below 25%, as well as exceptionally good overall properties which make them especially useful in gaskets, flexible hose, and the like. Certain of the coagents, such as the acrylate esters and the allylic cyanurates, are less compatible with the chlorinated polyethylenes than are the diallyl esters, but are very effective in minor amounts between 0.5 and 20 parts in producing cured chlorinated polyethylene elastomers of low compression set, high tensile strength and excellent overall properties. Such coagents are effective both in unfilled gum stock and filled compositions suitable for wire jacketing, gaskets, hose and the like. These coagents are also effective in plasticized or oil extended chlorinated polyethylene, and especially in chlorinated polyethylenes extended with chlorinated hydrocarbons such as the chlorinated paraffin waxes which may be used to facilitate mixing of the coagent with the chlorinated polyethylene. The coagents such as the acrylates and triallyl cyanurates are preferably employed in amounts between 1 and 15 parts, the upper limit depending largely on the limits of compatibility with the chlorinated polyethylene. It is generally desirable not to exceed substantially the limits of compatibility or miscibility, as this tends to interfere with the subsequent cure and cross-linking treatment and also to lower the processibility of the mixture. Polyfunctional coagents based on the acrylates, triallyl cyanurates, divinyl benzene, and the like, even though employed in minor amounts, are effective thermal stabilizers for chlorinated polyethylene. (see Examples 12—15). These coagents may also be employed in bonding thermoplastic and elastomeric materials in accordance with the invention.

The compositions of the invention include a free radical-generating addition polymerisation initiator. Free radical initiators effective to cause polymerization of the coagent are well known, examples being silver peroxide, the perborates, the percarbonates, benzoyl peroxide, dicumyl peroxide, butyl-α-cumyl peroxide, *o,o*-dichlorobenzoyl peroxide, diphenylcyclohexyl peroxide, butyltriphenyl methyl peroxide, *o,o*-dibromobenzoyl peroxide, di-butyl peroxide, diacyl peroxides, 2,5 - bis - butyl peroxy - 2,5 - dimethyl) hexane, butyl hydroperoxide, cumene hydroperoxide, lauroyl peroxide, 2,5 - dimethyl-2,5 - di(- butyl peroxy) - hexyne - 3, 1,4 di - t - butyl peroxy diisopropyl benzene, tetralin peroxide, *para*-menthane hydroperoxide, diisopropylbenzene hydroperoxide, as well as other polymerization catalysts including the diazo compounds and the like. The particular initiator used will be chosen having regard to the processing temperatures used in compounding to avoid premature curing on the mill. It is also desirable to selector an initiator which by itself is among the more highly effective cross-linking or curing agents for chlorinated polyethylenes of 15—50% chlorine content. The more preferred initators or polymerization catalysts are the tertiary organic peroxides such as di-α-cumyl peroxide. The amount of the initiator employed may vary, but will usually be between 0.3 and 20 parts per 100 parts of chlorinated polyethylene, and preferably 2 to 12 parts.

The compositions of the invention may include filler material to reduce their cost, balance properties and produce products adapted for specific end uses. Any of the well known filler materials may be used, examples of the more suitable fillers including the carbon blacks such as furnace black, channel black, thermal black, lamp blacks and the like, silica, titanium dioxide, mica, aluminas, hydrated aluminas, clays, carbonates such as magnesium and calcium carbonate and talc. The amount of filler incorporated in the compositions may vary widely, being generally between 20 and 200 parts or more, preferably for most product applications between 40 and 175 parts, per 100 parts of chlorinated polyethylene. Finely divided carbon black, carbonates, hydrated alumina, and the talcs are illustrative of preferred fillers.

The compositions of the invention may include other additives such as plasticizers, extenders, stabilizers and anti-oxidants, as desired or required for a particular purpose. While the allylic compound may serve as a plasticizer during compounding, the polymerized allylic material has much less plasticizing effect, and hence additional non-

polymerizable plasticizing material may be added to reduce hardness or adjust other properties of the cured product. Examples of the more suitable plasticizers or extenders include the highly aromatic oils, naphthenic oils, chlorinated aliphatic and aromatic hydrocarbons, epoxidized oils such as epoxidized soya bean oil, and di-ester plasticizers derived from alcohols having 4 to 16 carbon atoms and such acids as phthalic, adipic and sebacic. The chlorinated hydrocarbons are well known plasticizers which represent one group of preferred plasticizers. They may be aliphatic or aromatic; mixtures of two or more may also be used. The chlorinated hydrocarbon extenders generally have a chlorine content between 20% to 70% and a low molecular weight, between 200 and 2,000. The preferred chlorinated hydrocarbons are normally liquid materials of molecular weight between 200 and 1,000, especially those of chlorine content about 30% to 55% and molecular weight about 300 to 1,000. Amounts of plasticizer may vary widely between say 5 and 100 parts, preferably 10 to 50 parts, per 100 parts of the chlorinated polyethylene.

While the preferred allyl phthalate acts as a heat stabilizer during processing of the uncured composition, it undergoes polymerization during curing and the final material is apparently less effective as a heat stabilizer in the cured products. Hence, it may be desirable to add further heat stabilizers which are fully effective in the cured compositions. Several stabilizers are well known to be effective for chlorinated polyethylene compositions including, by way of illustration, the inorganic salts and organic complexes and salts of metals such as barium, cadmium, tin, zinc lead and sodium. Also especially suitable are the liquid epoxy resins such as epoxy tallate, and those prepared by reaction of epichlorohydrin and Bisphenol A. The amount of such heat stabilizer added is usually about 1 to 15 parts, especially 3 to 10 parts, per 100 parts of the chlorinated polyethylene. The preferred stabilizer is an epoxy tallate, which serves also as a plasticizer or processing aid.

The compositions of the invention may be prepared by any suitable mixing procedure, such as those conventionally employed in rubber compounding. In a preferred procedure the chlorinated polyethylene, along with the other components of the desired composition except the initiator, is charged to a suitable mixer such as a Banbury mixer preheated to a temperature preferably between 130°F. and 200°F. Mixing is continued at temperatures between about 150°F. and 400°F., preferably 200°F. to 320°F., the mass being heated by supplying heat through the mixing apparatus and/or by the frictional heat of mixing generated when substantial amounts of filler are included in the charge. The initiator is preferably added at a time when there is not more than about 4—5 minutes, preferably 1—3 minutes, of mixing remaining before discharge of the composition from the mixer, desirably after adjusting the temperature of the mass or stock to about 240°F. or below, or in any event well below the initiation or polymerization temperature of the coagent; a temperature between 180°F. to 230°F. will usually be preferred. The total mixing time may range generally from 3 minutes up to about 15 minutes or more. It has been found that thorough and complete mixing of the chlorinated polyethylene and coagent compound to form a homogeneous mass is important for obtaining optimum results in the finally cured product, and especially affects final properties such as tensile strength and compression set. The preferred total mixing time is about 6 up to 15 minutes. When using the preferred high molecular weight chlorinated polyethylene having an intrinsic viscosity of 2.5 to 6, it is especially important to conduct the mixing for at least some substantial period at a temperature above 200°F. in order to obtain an effective mixture of the chlorinated polyethylene and coagent and any plasticizers or extenders which may be added, and preferably at a temperature of about 240°F. to 320°F. over the major portion of the mixing period before adding the initiator. The compounded mass after mixing in the initiator is discharged from the mixer and may be formed into sheets, as for example on a two-roll rubber mill, and such sheet divided up in a conventional manner for moulding or extrusion, and final cure of the composition. Alternatively, the chlorinated polyethylene may be mixed with the allylic compound and any optional ingredients, excepting both substantial amounts of fillers and the initiator, on a suitable mixer such as a two-roll rubber mill, to produce sheets of the mixed homogeneous composition, similar to uncured gum stock, which may be stored or shipped for subsequent compounding and addition of fillers and initiator. In producing such uncured stock diallyl phthalate may be employed as the heat stabilizer, and offers the advantage of producing a storable and/or saleable product which may be later compounded with other ingredients including a heat stabilizer more specifically selected according to the particular application in which the final cured elastomer will be used.

The compositions of the invention may be cured generally at temperature of about 160 to 450°F. under pressures of the order of 50 to 1,000 p.s.i., and even higher. Preferably, the curing is carried out at a temperature of about 300—400°F. at a pressure between about 300 and 800 p.s.i. The curing time may be between about 1 and 60

minutes, and is usually 10 to 30 minutes. In addition to being suitable for moulding, the filled compositions of the invention are eminently suited for wire jacketing, and in the form of strips or the like may be fed to an extruder and extruded therefrom as a jacket over copper wire and the like in a conventional manner. Extrusion temperatures are usually about 180°F. to 250°F. The jacketing may be vulcanized or cured by application of heat and pressure in convenional equipment such as a continuous steam vulcanizer in which the temperature is usually between about 350°F. and 420°F. and the steam pressure between about 180 and 240 p.s.i. The compositions of the invention have been found to have the advantage of being extrudable to form products not subject on final curing to stress cracking which has been a problem heretofore in extruding many compositions based mainly on chlorinated polyethylene.

The especially preferred chlorinated polyethylenes of intrinsic viscosity between about 2.5 and 6.0, preferably 3 to 5, may be obtained by chlorination of a substantially linear, high density polymer of ethylene having a very high molecular weight of at least about 500,000 and up to about 5,000,000, preferably about 1,000,000 to 3,500,000, calculated according to the method of P. S. Francis *et al* from the viscosity of a 0.5 to 0.1 gram per 100 cc. solution in decalin at 135°C., using the equation:

$$n=6.77\times10^{-4}M^{0.67}$$

where

n=intrinsic viscosity

M=weight average molecular weight

(J. Polymer Science Vol. 31, pp. 453—466 — September, 1958).

Particularly suitable linear high molecular weight polyethylene, which may also be characterized by containing long chain polyethylene branches, is produced, as described in our British Specification No. 858,674, by gas phase polymerization of anhydrous, oxygen-free ethylene below the softening point of the polyethylene over a porous, frangible catalyst consisting of an inorganic compound of chromium and oxygen and an active metal alkyl on a support of silica or silica-alumina. The polyethylenes so produced contain residues of the chromium-silica catalyst systems dispersed throughout the polyethylene in an amount of at least about .001%, usually .001—.002%. This chromium-silica catalyst material is retained in the polyethylene during chlorination and contributes to the properties of the chlorinated polyethylene and of the elastomeric compositions produced therefrom. Prior to chlorination the polyethylene from which the chlorinated polyethylene is made has a density between about 0.935 and about 0.985 gm/cm³ at 23°C. and a crystallinity of at least 75% and customarily in the range 75% to 90%, as measured on a carefully annealed sample by an absolute method, e.g. by infrared spectrum analysis or by X-ray analysis. The DTA crystalline melting point, i.e. the maximum in the differential thermal analysis peak produced by the polyethylene starting material, is at least 125°C., and at least 90% of the area of this peak is produced at temperatures of 110°C. and above.

Chlorinated polyethylene of less than 1% crystallinity is desirably prepared for use in the invention by chlorination of the high molecular weight polyethylene in a heterogeneous medium in stages defined by introduction of chlorine at a temperature first below and then above the crystalline melting point of the polymer, as described in British Specification No. 950,374, most desirably by a two-stage suspension chlorination of the linear, very high molecular weight polyethylene, in which the first-stage chlorination is carried out in an aqueous slurry at a temperature below the crystalline melting point of the ethylene polymer, preferably about 60°C. to 130°C., and especially 90—110°C., until at least about 5 percent, preferably about 10 percent, of chlorine has been introduced into the polymer. In the second stage the chlorination is continued in the aqueous slurry at a temperature maintained above the crystalline melting point of the polymer but below the softening point of the chlorinated outer coating thereof until the desired total amount of chlorine has been added. Second-stage chlorination temperatures are at least about 135°C. and preferably 135°C. to 150°C. If desired, chlorination in the second-stage may be carried out at a temperature above the crystalline melting point of the polymer for a time sufficient to add at least about 5 percent chlorine and preferably give a total of at least 25 percent chlorine, and then continued at a lower temperature, e.g. 110°C. to 120°C., until the product has the desired final chlorine content.

The following Examples illustrate the invention.

Example 1

Chlorinated polyethylene of 40% chlorine content was prepared by chlorination of polyethylene of average molecular weight 1.2 million, corresponding to an intrinsic viscosity of about 1.5 dl/gm, and melt index (ASTM D1238—52T; 190°C., 2160 gm weight) of about 0 gm/10 min. The polyethylene was prepared by gas phase polymerization of an anhydrous oxygen-free ethylene over a catalyst of magnesium dichromate on a porous support of 90% silica and 10% alumina with aluminium triisobutyl, prepared in accordance with Examples 6 of British Specification No. 858,674. The polyethylene contained about

0.015% by weight residue of the magnesium dichromate/silica-alumina catalyst. The polyethylene, at a particle size such that 100% passed through a 50 mesh standard screen, was slurried in about 20 times its weight of water containing a non-ionic surface active agent in an enclosed vessel provided with means for heating and cooling and for turbulently agitating its contents, and with a thermowell and thermocouple to measure the slurry temperature. The chlorination was commenced and maintained at a temperature of about 100°C. until the product contained 17% by weight of chlorine, and was then continued at 140°C. until the chlorine content reached 40% by weight. The feed rate of chlorine was about 0.2 lb. of chlorine per hour per lb. of polyethylene charged throughout these operations. During the chlorination the total pressure ranged up to about 16 psig.

The resulting slurry was filtered, and the chlorinated polyethylene product dried at a temperature of 60°C. for 24 hours. It had a chlorine content of 40%; and contained 0% of material showing polyethylene crystallinity, as determined by differential thermal analysis according to the procedure outlined hereinafter. The glass transition temperature was about −15°C., as determined by stiffness modulus (according to ASTM D1053-61), reaching 10^9 dynes/cm^2 at this temperature. The molecular weight corresponded to an intrinsic viscosity of 4.0 in *o*-dichlorobenzene at 100°C.

The dry chlorinated polyethylene resin (100 parts) was poured onto a two roll rubber mill preheated to 200—220°C. along with 40 parts of diallyl phthalate. The charge was blended on the mill for about 6 minutes to form a homogeneous mass, after which 2.8 parts of di-α-cumyl peroxide was added and mixing continued for an additional two minutes. The blended composition was then sheeted out at a thickness of about 0.085 inch. The sheet was cut into 4×5 inch slabs and the slabs inserted into a suitable mould which was placed in a press where the slabs were cured at a pressure of 500—600 p.s.i. and at a temperature of 150—160°C. for a period of about 20 minutes. The resulting cured product resembling an unfilled cured gum stock was then evaluated as to gel content and physical properties, with the results tabulated in Table 1. Also given in Table 1 for purposes of comparison are the properties of two additional compositions prepared on a two roll mill similar to that of Example 1 and constituted as follows:

Control A

This composition contained 100 parts of the chlorinated polyethylene of Example 1, 4 parts of an epoxy heat stabilizer prepared by reaction of epichlorohydrin with Bisphenol A ("Epon" 828), 3 parts carbon black, and 1 part of an anti-oxidant. This mixture was prepared essentially to determine the properties of the basic chlorinated polyethylene resin.

Control B

This composition contained 100 parts of the chlorinated polyethylene of Example 1, 4 parts of "Epon" 828, 7 parts of di-α-cumyl peroxide, and 1 part of an anti-oxidant. The slabs of the blended composition were moulded in a press at a pressure of 500—600 p.s.i. and temperature of 150—160°C. for about 20 minutes.

Table 1

Property	A	B	Ex. 1
Gel Content		94%	94%
Tensile Strength	1745	2060	3700
Elongation, %	465	340	400
300% Modulus, p.s.i.	500	1900	2000
Shore A Hardness	60	56	70
Mooney Viscosity (100°C.)			65
Dielectric Strength, vpm			630
Water Pick-up, mg/in²			18.2
Compression Set, %			25
Low Temperature Impact, °C.			−36
Tear Strength, Trouser, lb/in			73

Thus the composition of the invention as illustrated by Example 1 has a gel content of 94% and high modulus, confirming a high degree of cure of the chlorinated polyethylene and the cross-linking thereof through the diallyl phthalate. The cured composition of Example 1 also has a surprisingly high tensile strength of 3700 p.s.i., substantially better than the straight peroxide cured control composition A and almost double that of the basic resin as represented by control composition B. The composition of Example 1 also has other desired properties, including a compression set value of only 25%.

EXAMPLE 2

Filled compositions were prepared by first charging 100 parts of the chlorinated poly-

ethylene of Example 1 to a Banbury mixer, Model B, preheated to 140—160°F. along with 20 parts diallyl phthalate, 30 parts of epoxy tallate ("Nuostab" 828; "Nuostab" is a registered Trade Mark), 150 parts of platey talc ("Mistron Vapor"; "Mistron" is a registered Trade Mark), 2 parts of vinyl silane as filler bonding agent (Vinyl Silane 172), and 1 part of polymerized trimethyl dihydroquinone ("Age Rite Resin D"). The resulting stock was blended on the mill for about 8 minutes to form a homogeneous mass. There was then added 3 parts of di-α-cumyl peroxide and after an additional 2 minutes of mixing the stock was sheeted out on a two roll rubber mill at a thickness of about 0.08 inch. The sheet was cut into 4×5 inch slabs and inserted in a mould which was placed in a press where the slabs were cured at a pressure of 500—600 p.s.i. and at a temperature of 150—160°C. for a period of about 20 minutes. The cured product was evaluated as to gel content and physical properties, with the results tabulated in Table 2.

Table 2

Property	Ex. 2
Gel Content	94%
Tensile Strength, p.s.i.	1850
Elongation, %	425
300% Modulus, p.s.i.	1500
Shore A Hardness	75
Mooney Viscosity (100°C.)	100
Dielectric Strength, vpm	600
Water Pick-Up, mg/in²	12.5
Compression Set, %	20
Low Temperature Impact, °C.	—36
Tear Strength Trouser, lb/in	73

The high gel content and high modulus confirm a high degree of cure of the chlorinated polyethylene. The composition also has high elongation and good tensile strength of 1850 p.s.i. Of special interest is that the highly filled composition shows a compression set value of only 20%.

EXAMPLE 3

A filled low cost wire jacketing composition was prepared by first charging 100 parts of the chlorinated polyethylene to a Banbury Mixer, Model No. B, operated at a speed of about 110—120 r.p.m. and preheated to a starting temperature of about 160°F. by internal steam heating. To the chlorinated polyethylene there was immediately added 12 parts of diallyl phthalate and 30 parts of a chlorinated aliphatic hydrocarbon of chlorine, content 40%, and molecular weight about 580 ("Chlorowax" 40; "Chlorowax" is a registered Trade Mark). The resulting mass was allowed to work on the Banbury mixer for about ½ minute and there was then added 1 part of polymerized trimethyl dihydroquinone ("Age Rite D"), 50 parts of the platey talc, and 100 parts of carbon black ("MT Black"). After such addition the temperature of the mass increased rapidly to about 250—260°F. and a homogeneous mixture was formed in about 8 minutes after such addition. Cooling water was then applied externally to the Banbury mixing chamber jacket to decrease the temperature of the stock to between about 230—240°F. and there was then added 8 parts of di-α-cumyl peroxide. The stock was allowed to mix for an additional 2 minutes at a temperature of 220—230°F., and was then sheeted out as a 0.08 inch thick mat on a two roll rubber mill. Slabs 4×5 inch were cut from the mat, and the balance of the mat cut into strips. The slabs were cured in a press mould as in the preceding Examples and the resulting product evaluated with the results reported in Table 3. The strips cut from the mat were employed as charge to a 14:1 L/D ratio J. Royle & Sons Company extruder, Model No. 1, from which the compound was extruded at a temperature of about 200—220°F. onto 145 tinned copper wire with a 3/64 inch wall. The extrudate was passed to a continuous steam vulcanizer where the coating was cured by subjecting it to a temperature of about 400°F. at a direct steam pressure of about 200 p.s.i. for 3 minutes. The cured coated wire was water cooled and was found to be free of stress cracking which is encountered upon extrusion and vulcanization of compositions similar to that of this Example but prepared without the inclusion of the diallyl phthalate. In Table 3 the pressed moulded slabs are evaluated according to the specifications for wire jacketing of the Underwriters' Laboratories (UL).

Table 3

Original Vulcanizate	Ex. 4	U.L. Specification
Tensile strength, p.s.i.	2000	1800
Elongation, %	475	300
After 20 hrs. at 127°C. in Air Press Bomb		
Tensile strength, p.s.i.	2000	50% of orig.
Elongation, %	450	150%
After 18 hrs. at 121°C. in ASTM oil No. 2		
Tensile strength, p.s.i.	1800	60% of orig.
Elongation, %	375	60% of orig.
After 240 hrs. at 121°C. in circulation Air Oven[1]		
Tensile strength, p.s.i.	1800	900
Elongation, %	350	50%

[1] Sample Press Cured at 205°C. for 2 minutes.

The chlorinated polyethylene - diallyl phthalate vulcanized jacketing of the invention not only clearly satisfy the above standards but retain them extremely well on heat and oil aging. In addition to the above properties, which include exceptional oil resistance, the jacketing was also found to have others especially high tear strength, good ozone resistance, and non-flammability. Gel content was 94%, and Water Pick-Up 12.9%. A similar composition prepared without the diallyl phthalate shows substantially high compression set and substantially reduced tolerance in the oil aging test.

EXAMPLE 4

A filled heavy duty non-black wire-jacketing was prepared by charging 100 parts of the chlorinated polyethylene of the preceding Examples to a Banbury mixer along with 30 parts of the epoxy tallate "Nuostabe" 850, 20 parts of diallyl phthalate, 150 parts of hydrated alumina ("Hydral" 710), 2 parts of Vinyl Silane, and one part "Age Rite Resin D". The charge was admixed as in Example 3, the temperature rapidly increasing to about 250—260°F., to form a homogeneous mixture after about 8 minutes of mixing. Cooling water was then applied externally to the Banbury mixing chamber jacket to decrease the temperature of the stock to, 220—230°F. and there was then added 7 parts of di-α-cumyl peroxide. The stock was allowed to mix an additional 2 minutes at a temperature of about 230°F. and was then sheeted out as a 0.75 inch thick mat on a two roll rubber mill. Following the procedures of Example 3, slabs were cut from the mat for test purposes while strips cut from the mat were extruded onto tinned copper wire and cured in a continuous steam vulcanizer at a temperature of about 400°F. at a direct steam pressure of about 220 p.s.i. for 3 minutes. The properties of the cured composition and stress crack-free extrudate are reported below in Table 4.

Table 4

Vulcanizate	
Compounded Viscosity, ML-4 at 212°F.	100
Mooney Scorch, MS at 250°F.	
Minimum	45
Minutes to 5 pt. rise	22
Original Properties	
Tensile Strength, p.s.i.	1850
Elongation, %	425
300% Modulus	1500
Heat Aged 7 days at 250°F.	
% Tensile strength Retained	100
% Elongation Retained	70.5
Oil Aged 18 Hours at 250°F. in ASTM No. 2	
% Tensile Strength Retained	122
% Elongation Retained	70.5
Oxygen Bomb Aged, 168 Hours at 80°C.	
% Tensile Strength Retained	94.5
% Elongation Retained	86.0
Tear Strength	
Trouser, lb/in	73
Water Absorption	
Mg/in[2]	12.5
Low Temperature	
ASTM D-746	−36°C.
Compression Set, Method B	
22 Hrs. at 212°F., %	20

Example 5

A cured elastomer was prepared by a procedure similar to that of Example 2 with 100 parts of the same chlorinated polyethylene and 40 parts of diisoallyl phthalate, 7 parts of di-α-cumyl peroxide, 1 part of "Age Rite Resin D" as anti-oxidant, and 60 parts of the hydrated alumina. Results and physical properties of the products are tabulated below in Table 5.

Table 5

Original Properties	
Tensile Strength, p.s.i.	2750
Elongation, %	365
300% Modulus	2550
Shore A Hardness	76
Heat Aged 7 days at 250°F.	
Tensile Strength, p.s.i.	3300
Elongation, %	250
Shore A Hardness	85
Compression Set, Method B	
22 Hrs. at 212°F., %	17

Example 6

A cured elastomer was prepared as in Example 5 except that 40 parts of diallyl maleate was employed as the diallylic compound. Results and physical properties of the product are similar, as recorded in Table 6.

Table 6

Property	
Tensile Strength, p.s.i.	2850
Elongation, %	200
Shore A Hardness	83
Compression Set, %	9.1
Heat Aged 7 days at 250°F.	
Tensile Strength, p.s.i.	3200
Elongation, %	125
Shore A Hardness	91

Example 7

A cured elastomer was prepared as in Example 5 except that 50 parts of diallyl phthalate prepolymer ("DAPON" 35; "Dapon" is a registered Trade Mark), was substituted as the diallylic compound. Results and physical properties of the products are tabulated below in Table 7.

Table 7

Original Properties	
Tensile Strength, p.s.i.	3000
Elongation	150
300% Modulus	
Shore A Hardness	94
Heat Aged 7 days at 250°F.	
Tensile Strength, p.s.i.	3025
Elongation	150
Compression Set, Method B	95
22 Hrs. at 212°F., %	11.6

In Example 1, although the chlorinated polyethylene was mixed with the diallyl phthalate on the rubber mill for several minutes at a high temperature above 200°C. in the absence of a separate heat stabilizer for the chlorinated polyethylene, the chlorinated polyethylene did not substantially change colour or darken, as normally occurs when chlorinated polyethylene is heated to such temperature for such a time in the absence of a heat stabilizer. Evaluation of the stock discharged from the rubber mill confirmed the value of the diallyl phthalate as a heat stabilizer for the chlorinated polyethylene. Examples 5, 6 and 7, employing respectively diisoallyl phthalate, diallyl maleate and the diallyl phthalate prepolymer were also carried out in the absence of a separate heat stabilizer and also demonstrated the stabilising effect of such diallylic materials, not only by observation of the stock during Banbury mixing but also by results obtained after heat aging of the heat cured products, which showed a high degree of retention of physical properties. It was further evident that the beneficial heat stabilizing properties of the diallylic compounds were retained, at least to some extent, in the cured products containing the polymerized diallylic material.

A very advantageous and unexpected utility of the chlorinated polyethylene compositions of the invention has been discovered in the bonding of thermoplastic materials and elastomers, including natural and synthetic rubber. When the uncured compositions containing the chlorinated polyethylene, diallylic compound and free radical initiator are placed in contact with another thermoplastic or elastomeric resin and subjected to heat and pressure sufficient to cure the composition, it was found that a laminate of very high peel strength was produced. No explanation can be offered with certainty for such beneficial result, although it is believed that some of the allylic material, probably along with some of the free radical initiator, migrates from the chlorinated polyethylene composition at and into the interface of the assembly, and probably also into the adjacent resinous member, and results in a linkage between the materials being bonded upon polymerization of the polyallylic compound. That the bonding is more than a mere cross-linking between the materials is shown by the relatively small amounts of curing agent in the chlorinated polyethylene compositions, and the excellent results obtained with thermoplastic resins not commonly cross-linked by the free radical initiators. While migration into the adjacent material is believed to take place, it is not essential to compress the assembly during bonding at a temperature above the softening point or crystalline melting of the adjacent material, as evidenced by success with cured elastomers and a temperature below the melting point of thermo-

plastic material. However, better results are obtained as temperatures increase, and it is usually preferred to bond thermoplastic resins at temperatures above the softening point. The bonding properties of the compositions of the invention may be utilized to form laminates of two or more plies for a variety of uses including plastic upholstery, plastic flashing, and elastomer applications generally.

An allied effect of special interest and utility has been found in connection with wire coating and jacketing. In Examples 3 and 4 compositions provided by the invention were extruded onto wire as coating to demonstrate utility as a jacketing as well as coating. When similar compositions are extruded over wire already coated with, for example, a coating composition based on an ethylene-propylene terpolymer elastomer, a high strength bond is formed between the coating and jacketing. Such a result has been long desired in the wire and cable industry.

Any thermoplastic or natural or synthetic rubber material may be bonded in accordance with the invention. Merely illustrative of resinous materials with which excellent results are obtained are the polyolefins generally, including polyethylene and copolymers of ethylene with C_3 and C_4 olefins, including terpolymers of ethylene and propylene, vinyl chloride polymers and copolymers, polyvinylidene chloride, polychloroprene, polyacrylates, especially the flexible vinyl polymer compositions, polyamides such as nylon, polyesters, natural rubber, and synthetic rubber including butyl rubber. Generally, the resin containing the polyallylic compound may be further formulated in the general manner and in the varying proportions given for the chlorinated polyethylene elastomer compositions provided by the invention as hereinbefore described in detail. For example, either or both plies to be bonded may be formulated substantially without fillers or may contain filler materials up to the practical limits of filler loading.

The following Examples demonstrate the bonding of two such resin-based substrate compositions in accordance with the invention. In each, the composition containing the allylic compound was a chlorinated polyethylene composition formulated as in Example 4, and sheeted out to a thickness of about 30 mils. Laminates were evaluated as to bond strength by a pull test on a Tinius Olsen Instrument in which the laminate was subjected to a 180° peel and the pull required to separate the bonded plies is recorded.

Example 8

In this Example, the chlorinated polyethylene sheet or ply was bonded to a 30 mil thick sheet of peroxide cured polyethylene composition consisting essentially of 100 parts of a branched low density DYNH-1 polyethylene and 7 parts of di-α-cumyl peroxide. Bonding was effected by placing the sheets of chlorinated polyethylene and polyethylene in surface to surface contact and then subjecting the assembly to a temperature of 325°F. and pressure of about 200 p.s.i. in a mould press (ASTM slab mould) for about 30 minutes. Bond strength by the pull test on the Tinius Olsen Instrument was a high 100 pounds.

Example 8A

When Example 8 is repeated for purposes of comparison by omitting the diallyl phthalate from the chlorinated polyethylene composition and substituting therefor a plasticizing amount of a chlorinated low molecular weight paraffin, the peel strength of the assembly cured under the same conditions of temperature, pressure and time was only 4—10 pounds.

Example 9

Example 8 was repeated except that a 30 mil thick sheet of uncured polyethylene containing no curing agent was substituted for the cured polyethylene substrate of Example 8. Peel strength of the resulting bonded assembly was a high 100 pounds.

Example 9A

Example 9 was repeated for purposes of comparison, substituting a chlorinated paraffin for the diallyl phthalate as in Example 8A. Peel strength was 20—25 pounds.

Example 10

Example 8 was repeated except that a 30 mil thick sheet of nylon 6.6 having a softening point of 354°F. was substituted for the polyethylene substrate of Example 8. Peel strength of the resulting bonded assembly was a high 75 pounds.

Example 11

Example 8 was repeated except that a 30 mil thick sheet of an ethylene-propylene terpolymer elastomer (EPDM) was substituted for the polyethylene substrate. Peel strength of the resulting bonded assembly was a high 75 pounds.

The following Examples demonstrate the use of other coagents in improving the curing of chlorinated polyethylene and especially in forming cured elastomers of improved compression set, high tensile strength and high modulus.

Example 12

Cured filled compositions were prepared by the general procedure of Example 2 employing 100 parts of the chlorinated polyethylene of Example 1, 6 parts of "Epon" 828, 85 parts of a 40% chlorine content chlorinated paraffin wax ("Chlorowax" 40),

60 parts of carbon black ("FEF" Black), 3 parts of ditertiary organic peroxide ("S-890") as initiator and varying small amounts of triallylisocyanurate (TAIC) as the polyallylic compound. Cure time was 30 minutes at a temperature of 320°F. in each run. A control not containing an allylic compound gave the comparative results shown below for a composition containing 3 parts of triallyl isocyanurate.

	Control	3 Parts TAIC
Compression Set, 22 hr. at 212°F., %	32.5	17.8
300% Modulus	850	1200
Tensile Strength, p.s.i.	2300	2600
Elongation, %	575	500
Hardness, Shore A	52	53

Triallyl Isocyanurate

(Parts by Weight)

	1	2	5	10
Compression Set	21.5	17.5	16.2	13.8
300% Modulus	925	1100	1450	2000

Example 13

Cured filled compositions were prepared by the general procedure of Example 2 employing 100 parts of the chlorinated polyethylene of Example 1, 6 parts of "Epon" 828, 75 parts of ("Chlorowax" 40), 60 parts of carbon black ("FEF" Black), 3 parts of "S-890" as initiator, and varying small amounts of trimethylol propane trimethacrylate (TMPT) as the polyallylic compound. Cure time was 30 minutes at 320°F. in each run. The results obtained with a control not containing a polyallylic compound are compared below with those for a composition containing 3 parts of trimethylol propane trimethacrylate.

	Control	3 Parts TMPT
Compression Set, 22 Hr. at 212°F., %	32.5	20.3
300% Modulus	850	1250
Tensile Strength, p.s.i.	2300	2550
Elongation, %	575	500
Hardness, Shore A	52	54

Trimethyol Propane Trimethacrylate

(Parts by Weight)

	1	2	5	10
Compression Set	20.0	20.4	20.0	19.5
300% Modulus	1200	1230	1375	1500

Example 14

Cured filled compositions were prepared by the general procedure of Example 2 employing 100 parts of the chlorinated polyethylene of Example 1, 6 parts of "Epon" 828, 75 parts of "Chlorowax" 40, 60 parts of "FEF" Black, 3 parts of "S-890" as initiator and varying small amounts of ethylene dimethacrylate (EDMA) as the polyallylic compound. Cure time was 30 minutes at a temperature of 320°F. in each run. The results obtained with a control not containing a polyallylic compound are compared below with those for a composition containing 3 parts of ethylene dimethacrylate.

	Control	3 Parts EDMA
Compression Set, 22 hr. at 212°F., %	32.5	18.9
300% Modulus	850	1250
Tensile Strength, p.s.i.	2300	2700
Elongation, %	575	525
Hardness, Shore A	52	54

Ethylene Dimethacrylate

(Parts by Weight)

	1	2	5	10
Compression Set	19.3	19.0	16.3	14.5
300% Modulus	1225	1275	1500	1575

Example 15

Cured filled compositions were prepared by the general procedure of Example 2 employing 100 parts by weight of the chlorinated polyethylene of Example 1, 6 parts of "Epon" 828, 75 parts of "Chlorowax" 40, 60 parts of "FEF" Black, 3 parts of "S-890" as initiator and varying small amounts of divinyl benzene as the polyallylic compound. Cure time was 30 minutes at 320°F. in each run. The results obtained with a control not containing a polyallylic compound are compared below with those for a composition containing 3 parts of divinyl benzene.

	Control	3 Parts Divinyl Benzene
Compression Set, 22 hr. at 212°F., %	32.5	22.8
300% Modulus	850	1150
Tensile Strength, p.s.i.	2300	2550
Elongation, %	575	525
Hardness, Shore A	52	57

In the Examples, gel content is determined by placing a weighed 1/4×½ inch ×75 mil sample of the cured composition in a suitable vessel, in which it is immersed in 50 ml. of toluene at room temperature for one week; the gel content being indicated by the difference in the weight of the sample before and after the toluene extraction. The extracted sample removed from the toluene is blotted and oven dried at 105°C. to a constant weight, from which the determination of the gel content is finally made. Unless otherwise indicated, other properties are evaluated according to standard ASTM Tests, as follows: Tensile Strength, Elongation, and Modulus by D-412; Hardness by D-314-58; Trouser Tear by D-470-59T; Compression set by D-395-61; Low Temperature Impact by D-736-54T; Mooney Viscosity by D-1646-63; Oil Aging (liquid immersion) by D-471-63T; Oxygen Bomb Aging by D-572-61; and Heat Aging by D-573-53. Moisture absorption data were obtained using Underwriters Laboratory procedure — UL-44.

The crystallinity of the chlorinated polyethylenes is difficult to measure accurately by the conventional X-ray diffraction methods because the percent of the sample which shows crystallinity is low. It is, however, practical to measure the area under the DTA (differential thermal analysis) peak produced by the chlorinated polyethylene sample at about the melting point of the starting polyethylene, and compare this area with areas under the peaks similarly found upon a series of samples of various weights, taken from a sample like the starting polyethylene. The areas of the DTA peaks produced by such standard samples from any one source are found to be directly proportional to the weights of these samples. An estimate of the weight percent of material showing polyethylene crystallinity, contained in the chlorinated polyethylene, can then be obtained by measuring by an absolute method, such as X-ray examination, the proportion of crystalline material in the polyethylene employed as the source of the standard polyethylene samples. The DTA peak area can then conveniently be plotted against the weight of crystalline polyethylene material, whence weight percent of material showing polyethylene crystallinity, in any sample of known weight, can be immediately calculated. The crystallinities of the chlorinated polyethylenes referred to herein are so determined, and are essentially absolute crystallinities. Experiment has shown that the chlorinated polyethylene samples display their maximum crystallinity in their dry powder form, and that no annealing treatment is necessary or desirable prior to the DTA crystallinity determination.

WHAT WE CLAIM IS:—

1. A composition comprising (a) a chlorinated polyethylene, which is a homopolymer of ethylene or a copolymer of ethylene with up to 15 percent by weight of propylene or butylene and which contains 15 to 50 percent by weight of the chlorine, (b) at least 0.5 percent (based on the weight of the chlorinated polyethylene) of an organic compound containing at least two terminal ethylenically unsaturated groups each of formula

$$-\overset{|}{\underset{|}{C}}-CR=CH_2 \quad \text{or} \quad -\underset{\|}{C}-CR=CH_2,$$

in which R is hydrogen or an alkyl group, which, at least in the proportion employed, is compatible with the chlorinated polyethylene, and (c) a free radical-generating initiator for addition polymerisations.

2. A composition according to claim 1, in which the said organic compound is a diallyl phthalate.

3. A composition according to claim 1, in which the said organic compound is an acrylate of a polyhydric alcohol.

4. A composition according to claim 1, in which the said organic compound is divinyl benzene.

5. A composition according to any one of the preceding claims, in which the initiator is a tertiary organic peroxide.

6. A composition according to any one of the preceding claims, containing 7—15 percent (based on the weight of the chlorinated polyethylene) of the said organic compound.

7. A composition according to any one of claims 1 to 5 containing 15—70 percent (based on the weight of the chlorinated polyethylene) of the said organic compound.

8. A composition according to any one of the preceding claims, in which the chlorinated polyethylene has a chlorine content of 30—45 percent and a crystallinity less than 10 percent.

9. A composition according to any one of the preceding claims, in which the chlorinated polyethylene has substantially no crystallinity.

10. A composition according to any one of the preceding claims, containing also 20—200 percent (based on the weight of the chlorinated polyethylene) of a filler.

11. A composition according to any one of the preceding claims, containing also a plasticiser or extender.

12. A composition according to any one of the preceding claims containing also a

thermal stabilizer other than the said organic compound.

13. A composition according to claim 6 substantially as hereinbefore described.

14. A process for the production of a chlorinated polyethylene elastomer, which comprises subjecting a composition claimed in any one of the preceding claims to heat and pressure for a time sufficient to effect a substantial degree of cure thereof.

15. A process for effecting adhesion between two structures made of a thermoplastic or elastomeric resinous material, of which one is made of a chlorinated polyethylene composition as claimed in claims 1—13 which comprises placing the two structures together and subjecting the assembly to heat and pressure.

16. A process according to claim 15 in which the other structure is made of an ethylene polymer or a polyamide.

17. A process according to claim 16, in which the other structure is made of a peroxide-cured ethylene polymer or an elastomeric ethylene/propylene copolymer.

18. A process according to any one of claims 15 to 17, in which the said structures are sheets and a laminate of two or more sheets is formed from an assembly in which at least one of every adjacent pair of sheets is made of a composition as claimed in any one of claims 1 to 13.

19. Laminates obtained by the process claimed in Claim 18.

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